

Direct Methanol Fuel Cell for Portable Applications

T.I. Valdez, S.R. Narayanan, H Frank, and W. Chun
Jet Propulsion Laboratory, California Institute of Technology,
4800 Oak Grove Drive, Pasadena, CA 91109

Abstract

A five cell direct methanol fuel cell stack has been developed at the Jet Propulsion Laboratory. Presently direct methanol fuel cell technology is being incorporated into a system for portable applications. Electrochemical performance and its dependence on flow rate and temperature for the five cell stack are presented. Water transport data, and water transport mechanisms for direct methanol fuel cells are discussed. Stack response to pulse loads has been characterized. Implications of stack performance and operating conditions on system design have been addressed.

Introduction

The development of a direct methanol fuel cell system is presently being pursued at the Jet Propulsion Laboratory (JPL) under sponsorship from the Defense Advanced Research Project Office (DARPA).

A five cell methanol oxidizing stack has been developed at JPL. This stack incorporates liquid-feed direct methanol proton exchange membrane technology developed under an DARPA sponsored program [1, 2]. The direct methanol fuel cell stack (DMFC) operates by the oxidation of an aqueous solution of methanol to carbon dioxide at the anode and reduction of oxygen to water at cathode.

This paper focuses on results of parametric studies carried out on stacks. These studies form an important part of system development.

Background

Fuel cells have long been known as useful electrochemical storage devices, but have required large and complicated systems in order to operate. Upon the development of the direct methanol PEM fuel cell many system operating issues are simpler than before. In the DMFC, methanol can be oxidized directly at the anode, thus there is no need for fuel reformers. With the use of methanol fuel-water mixture, the PEM electrolytes are always at a high state of hydration. Using PEM electrolytes also allows for the operation without free-aqueous acid and thus less corrosion issues need to be addressed.

Membrane electrode assemblies (MEAs), the heart of the DMFC, consist of three main components; catalyzed anode, catalyzed cathode,

and a proton-conducting polymer electrolyte. The anode catalyst is Pt-Ru and the cathode catalyst is Pt. Nafion® 117 serves as the a proton-conducting polymer electrolyte (PEM).

The current state of technology at the single cell level for DMFC is 0.470 V at an applied current density of 150 mA/cm² for a cell running at 60 °C on air flow rate at ambient pressure. [3]

The following describes experimental results on the performance of the in-house built five cell DMFC stack.

Experimental

A description of the stack and its components is as follows: MEAs and all stack components were developed at JPL. The MEAs are prepared using 4 mg/cm² in-house Pt-Ru anode catalyst and 4 mg/cm² Johnson Matthey fuel cell grade Pt-Black cathode catalyst. The catalyst was applied on a porous carbon substrate and then bonded to a Nafion® 117 sheet. The active electrode area for each cell is 25 cm².

The stack biplates consist of machined graphite plates with a CVD coating of graphite. The reactants are fed to each cell in parallel. The flow fields in each biplate are of standard pin cushion design which allow for even fuel distribution and good electrode contact.

Two sets of experiments were carried out. The objective of these experiments was to establish stack performance capability under several operation conditions. The first set to determine electrical performance characteristics, and the second set focused on the rate of water production at the cathode due to electrochemical,

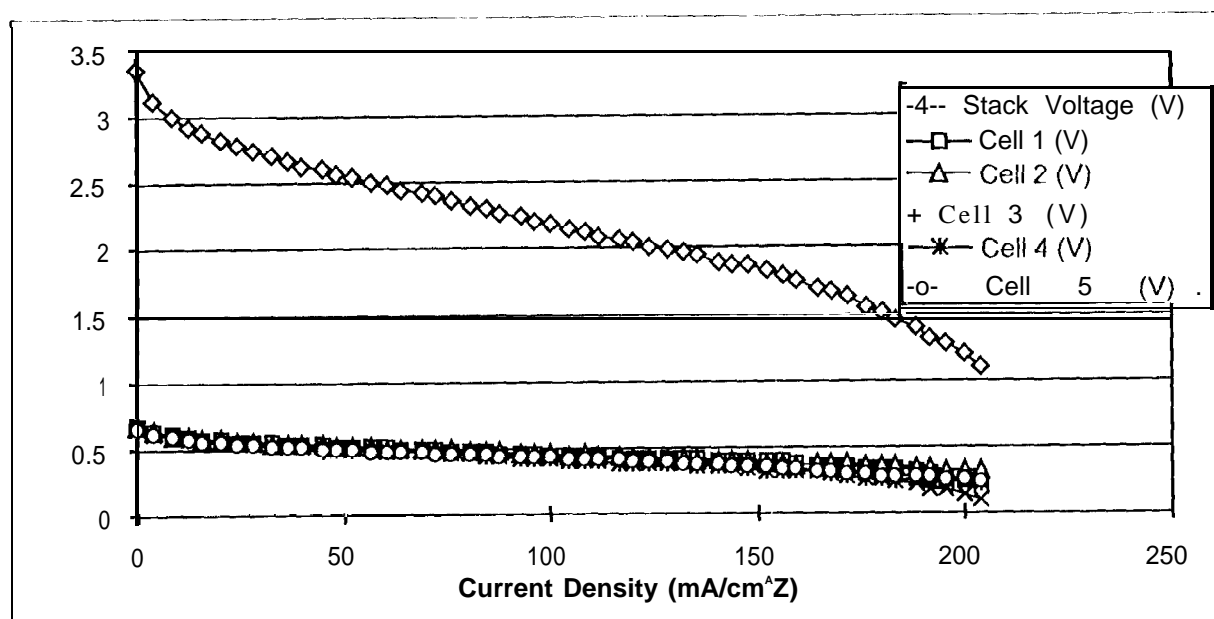


Figure 1. Five Cell DMFC Stack Electrical Performance with 60 °C, 1M Methanol, at 5 L/rein Air Flow Rate.

reactions and water transport across the membrane,

In the first set of experiments temperature was varied between ambient and 60°C and the flow rate was varied between one and five liter a minute. One of the engineering problems in the development of DMFC systems will be in cathode water management. The second set of experiments consisted of water collection studies at constant air flow rate and under applied current.

The results of these experiments are now described.

Results

A typical electrical performance curve is shown in figure 1. At low current densities, those below 50 mA/cm², the individual cell electrical performance varies only by a few mV. At current densities greater than 100 mA/cm² the variation from cell to cell is about 30 mV. With increasing current density we see the electrical performance of individual cells spread out, until some cells can no longer sustain the applied current density. At current densities above 200 mA/cm², the cells which could not sustain the applied current density go into reversal and thus begin to produce hydrogen at the cathode.

Several reasons can explain the performance of the stack. In general, cells towards the exit stream of fuels, share the greatest tendency towards poor performance. If a stack's fuel feed is in a series configuration, meaning that the fuels must travel through each cell, the cells towards the exit of the fuel feeds would in general have lower performance due to progressive depletion of reactant concentration while proceeding down the stack. In a stack with parallel fuel feed manifolds, and with a notable pressure drop within the flow fields, the individual cell performance loss as a function of position would be negligible. With just five cells and air flow of 5-8 times stoichiometric value, no variation in individual cell voltages is to be expected.

As mentioned earlier, at low current densities (< 50 mA/cm²) the cell voltages were very close to each other. However at applied current densities in excess of 150 mA/cm² it was observed that the two cells closest to the inlet of the fuel feeds performed on the order of 100 mV better than the worst cell in the stack. A random pattern was observed for performance loss for cells closest to the exit of the fuel feeds.

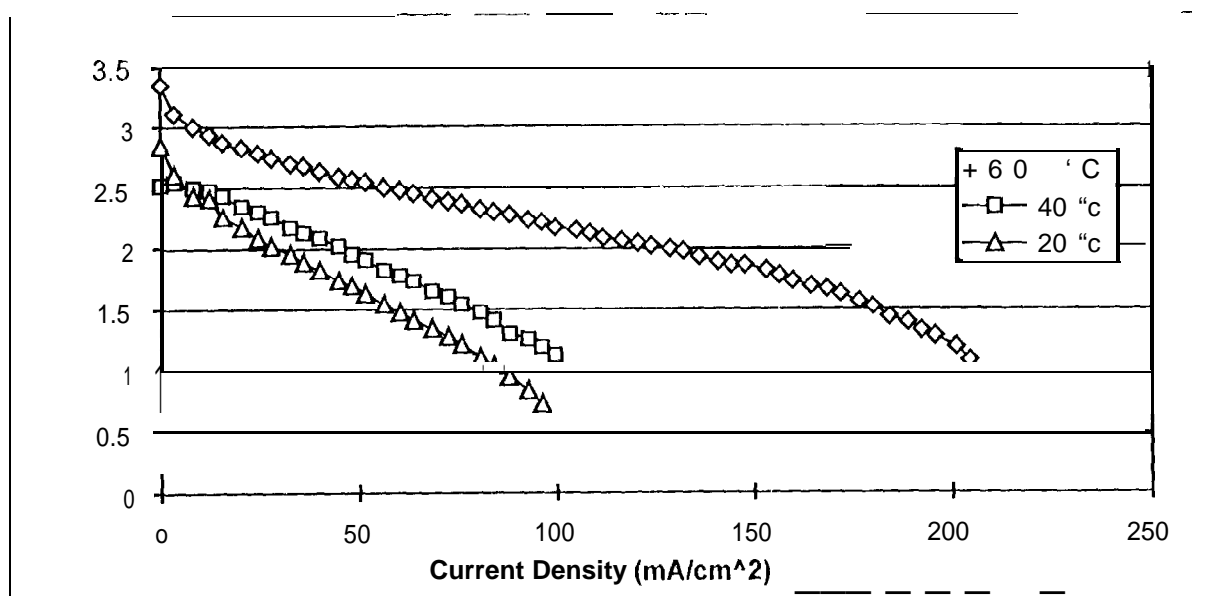


Figure 2. Five Cell DMFC Stack Electrical Performance at Various Temperatures, 1 M Methanol, at 5 L/rein Air Flow Rate

Water clogging of the outlet at each cell has been determined to be a major factor for performance loss in DMFC type stacks. This water clogging phenomena is only observed at higher current densities for two reasons; the stoichiometric delivery of oxygen becomes less at higher current densities and the rate of electrochemical water production is greater at high current densities. This water clogging phenomena is not observed in the cells nearest the inlet because the air flow rate is at it's highest pressure at the inlet, causing the flow to channel through the cells closest to the inlet, and effectively flushing water out from the cathode flow fields in these cells.

None of the cells are immune to this water clogging phenomena. At low stoichiometric rates and high current densities (thus high water production rates) any flow field may clog. Thus with an appropriately designed pressure-drop in the cathode flow fields and manifold, water removal can be improved and the range of operating current densities can be increased.

A strong dependence on temperature exists for the DMFC. At higher temperatures, catalytic activity is greater and proton diffusion rates through Nafion® 117 are greater. As can be seen from figure 2. The power density sustained at a particular stack voltage, say 2 V, nearly doubles

from 20 °C to 40 °C and then again doubles from 40 °C to 60 °C.

However there are always "trade-offs" to be considered in system design. Working at elevated temperatures may not be advantageous for certain system designs. In previous published articles [1,3] it has been shown that fuel cross over increases with increasing temperature thus leading to lower stack efficiency. High temperatures also increase water transported across the stack needing a bigger water management subsystem. Designing for portable power applications, it is sufficient to add more cells to increase stack power than to increase the operating temperature.

The influence of operating temperature on operating flow rate is presented in figures 3 - 5. All these experiments were performed at constant temperature at different flow rates. Figure 3, 4, and 5 are experiments at 20 °C, 40 °C, and 60 °C respectively.

At 20 °C anode performance of each cell is poor, however the stack is able to sustain operation at current densities well in excess of 50 mA/cm². Demonstrating **stack performance at ambient temperature is significant because it shows that DMFC is capable of low temperature operation** thus start-up issues are less problematic than fuel cells using reformers. Until

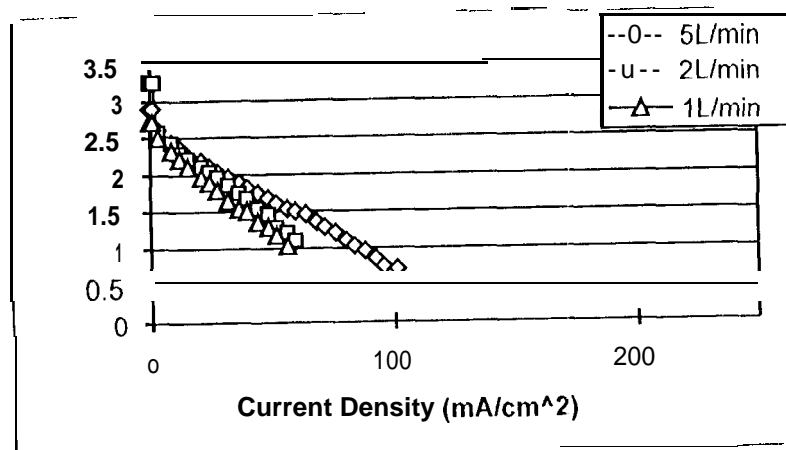


Figure 3. Five Cell DMFC Stack Electrical Performance at Various Flow Rates, 1M Methanol, at 20°C

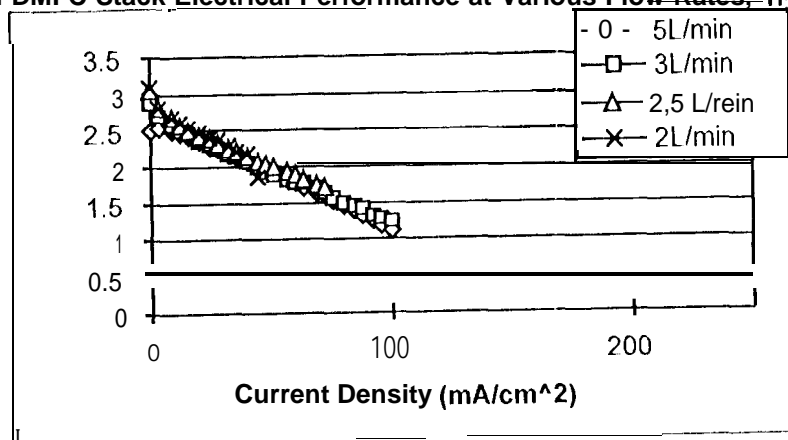


Figure 4. Five Cell DMFC Stack Electrical Performance at Various Flow Rates, 1M Methanol, at 400c

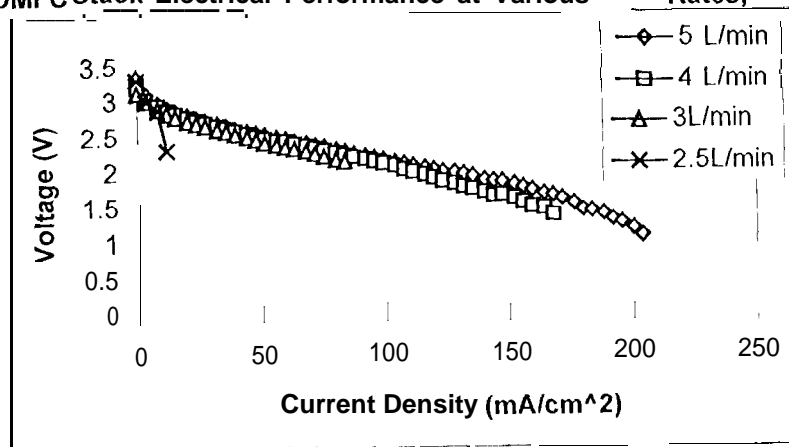


Figure 5. Five Cell DMFC Stack Electrical Performance at Various Flow Rates, 1M Methanol, at 60°C

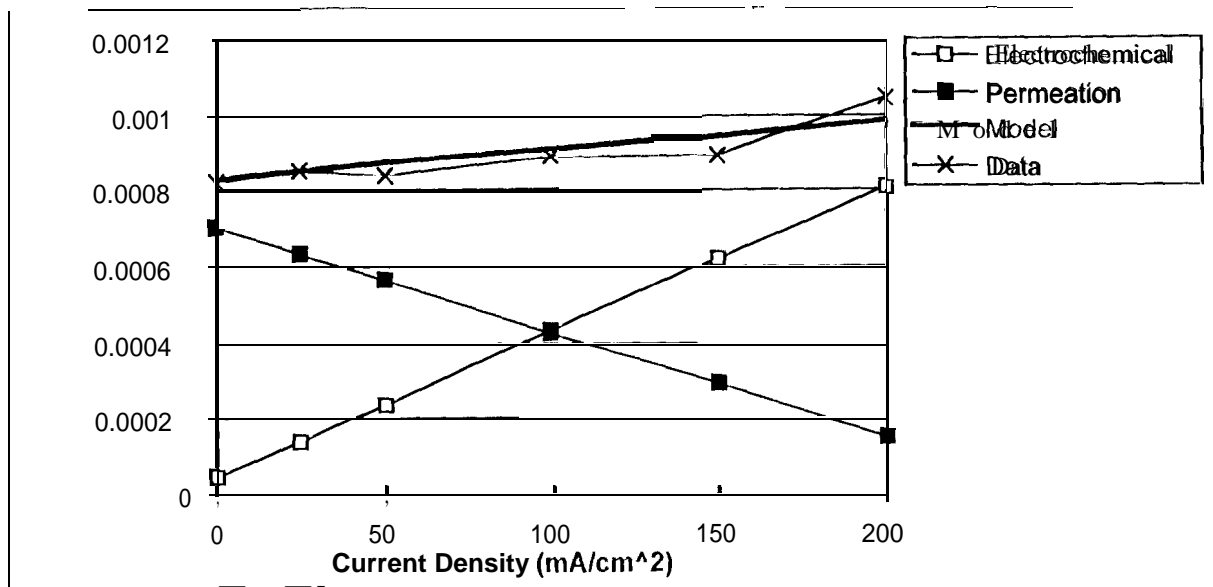


Figure 6. Five Cell DMFC Stack Water Transport Modeled.

recently [2] most disclosures of DMFC performance figures in the literature have always been for temperatures in excess of 90 °C and for flow rate many times stoic. in figure 3, it is seen that stable ambient temperature operation voltage of 1.2 V under a 50 mA/ cm² load with a flow rate just above 4 times stoic is achieved.

At elevated temperatures the need to provide greater air flows is apparent. As one raises the stack operating temperature from ambient to 60°C, the stack can no longer support current unless the air flow rate is appreciably increased. Comparing figures 3 and 5 we see that at ambient temperature, as mentioned above the stack could sustain a 50 mA/cm² load at a flow rate of 11./min, three times less of the flow rate required to sustain the same current density at 60°C.

Four modes of water transport exist in the stack namely; water produced electrochemically through applied load, water produced electrochemically due to cross-over, water crossover due to proton conduction (ElectroOsmotic Drag), and simple permeation.. The net flux from the four modes of water transport are given as:

$$N_{tot} = \frac{I}{n \cdot F} + \frac{Drag \cdot I}{n \cdot F} + \frac{I_{Cross}}{n \cdot F} + P_o + \frac{P_o}{C_{sat}} \cdot \frac{N}{F}$$

where I , is applied current, n moles from stoichiometry of individual reaction, $Drag$ is the drag coefficient, taken as 3, from literature [4] I_{cross} is the equivalent current due to fuel cross-over, F is Faraday's constant.

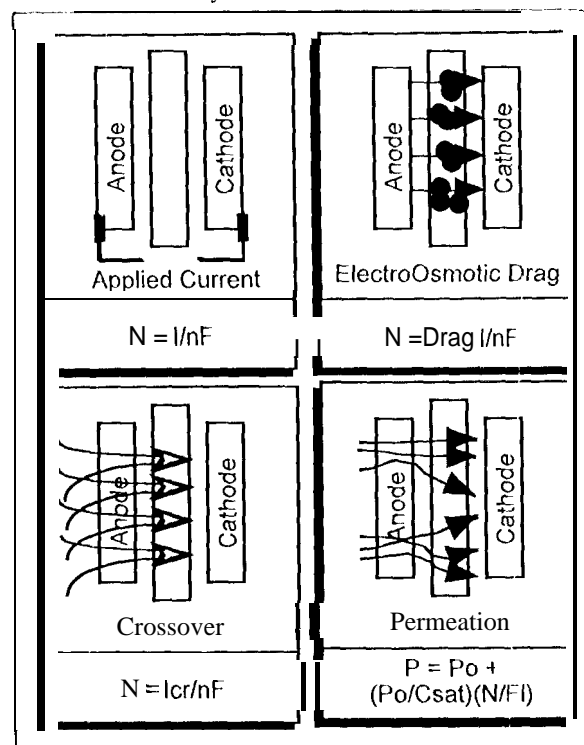


Figure 7. Four Modes of Water Transport..

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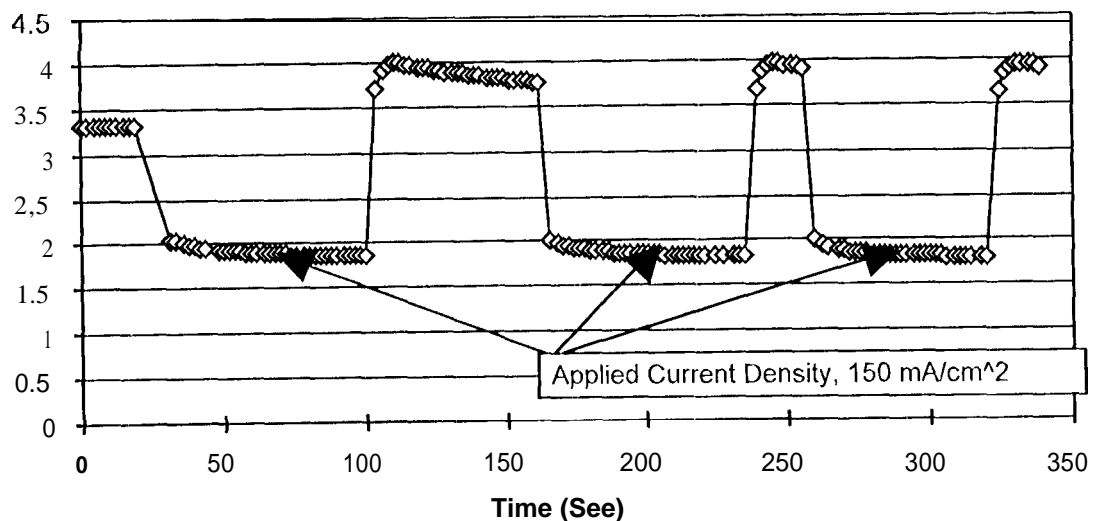


Figure 8. Five Cell DMFC Stack Pulse Performance at 60 °C, 1M Methanol, at 5 L/rein Air Flow Rate.

As shown in figure 6., the model is **validated** by experimental results. The typical water transport rates at 60 °C, with an air flow rate of 7.51 /min and an impressed load of 100 mA/cm² is 9×10^{-4} moles Of water/see. Water collection results are strong functions Of operating conditions as stated earlier. This experiment provides a measure of how much water will have to be condensed and returned to the system for water balance and thermal management

Figure 8. shows the stack response to applied load. The stack reaches a equilibrium voltage of 1.8 V under a 150 mA/cm² **applied load** on the order of 50 seconds. The stack exhibits no negative undershoot under applied load. The stack obtains a higher voltage at initial pulse prior to reaching a steady state.

Pulse performance as shown is important for many applications such as communication equipment, emergency back-up powersupply, and electric vehicles. The DMFC provides the necessary system response that can not be found in reformer type fuel cells simply because chemical processing equipment in the reformers are not very responsive

Conclusions

The development and testing of the DMFC stacks demonstrates practical use of this

technology. It was found that fuel cell stack performance is dictated by fuel flow fields and stack manifolds. Stack performance of 1.2 V at ambient temperature under a 50 mA/cm² load at flow rates just above 4 times stoichiometry **make** the DMFC practical for low power applications. Water transport experiments have given an understanding as to the factors contributing to cathode flow field water clogging phenomena.

Acknowledgments

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References

- 1-S.R.Narayanan, Proceedings of the 11th annual Battery Conference on Applications and Advances, Long Beach, CA., Jan 9-12, 1996. IEEE pg. 113-122
- 2- Koseck, J. A., Proceedings of IECEC'93, Atlanta, GA., Aug 8-13, 1993 pg. 1209 -1214 S.R.
- 3-Narayanan, Presented at the Fuel Cell Seminar, Orlando, FL., Nov 17-20, 1996. pg. 525 -528
- 4-Gotterfeld, S, Presented at Electrochemical Society Meeting, San Antonio, TX, Sept 22, 1996